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Optimization of Electrode Parameters of Stacked Structured Ultracapacitor

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Abstract

Energy crises are one of the biggest crises of the world today. With ever increasing gadgets and machinery required for a comfortable lifestyle the demand for more and more energy is on its peak. So the present energy consumption scenario demands a much smarter and efficient energy storing technology. Henceforth, we need to find some alternate and most important the efficient energy storage methods. We all know that the conventional storage devices of electrical energy like lead acid, lithium ion, nickel cadmium etc. that are available today suffer many drawbacks. But the major problem with the high scale use of these storage devices is less efficient method of energy storage. Electrode materials along with all the other input parameters play the most important role in deciding the output parameters of the ultracapacitor. This paper presents the optimization of electrode parameters for development of stacked type of aqueous based ultracapacitor.

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Keywords: Ultacapapcitor; Design of Experiment method; capacitance

1. Introduction

The objective of our research work was to study the effect of the quantity and quality of different parameters associated with electrode of the ultracapacitor. The scope of the work includes development of aqueous metal oxide based ultracapacitor through statistical modeling method. A large number of trials are conducted to observe the

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effect of varying input parameters on the output parameter of the ultracapacitor. For example, quantity of electrode material and type of current collector affects the capacitance. In this research work three parameters namely type ofactivated carbon, time of ultrasonic mixing and quantity of loading of electrode material on collector current as the basic input parameters have been considered. Hence a statistical method i.e. design of experiment method is used, which requires less number of trials. It gives a mathematical model, which predicts the capacitance of ultracapacitor for different values of these parameters.

At present ultracapacitor technology is under development stage. Energy density, power density and specific capacitance are required to be improved [1]. The capacitance per unit area can be enhanced significantly using material with high specific area and carbonaceous has high specific area and high capability to store charges [12]. When the carbonaceous compound are composites with metal oxide enhances its charge storing capacity [13]-[16]. Use of low cost effective material is also essential to make it techno-commercial product. Manufacturing aspects are not attended as companies manufacturing this device around the globe are very less [2]. Constructional issues, modeling and its power electronic based interface are at research stage. Some of these areas of this device have come in academic research. Industry research is also leading in this regard. It is found that researchers generally concentrate on internal resistance and capacitor of the ultracapacitor.

Ultracapacitors are generally used to supply high pulse current and not the pulse power. Pulse current depends on factors like electrode material, loading material, mixing time, type of electrolyte etc. We have considered all these factors and their effects on capacitance of the ultracapacitors in this work. Researchers from various branches have worked in this area. Some scientists like Adrew Burke, B E Convey, Nelms and Spykers have given significant contribution in this area. Parametric variation method such as design of experiment is very effective tool for analysis of ultracapacitor [3]. Various modeling methods have been tried [4]. Different parameters of the ultracapacitor like specific surface area, type of electrolyte, ultrasonic mixing time etc. has been taken as input [5] and the parameters like capacitance, internal resistance, pulse power etc. have been taken as an output in various models [6]. Different areas of engineering are broadly doing research work in the field of ultracapacitors such as: Metallurgy- worked to increase surface area, porosity, pore size distribution measurement, study of activated carbons and metal oxides[6]; Electrochemistry Groups- worked to increase power density, energy density, specific capacitance, volumetric capacitance, voltage etc., use of Nano-materials and composite materials [2][7]. Electrical Groups- worked for application of ultracapacitor with direct/ semi-active, fully active power electronic interfacing, modeling for the ultracapacitor applications etc. (work not suitable for device development [5]. Mechanical Groups- used in thermal modelling [8]. This method is not used by electrical engineers. This paper uses one of statistical method for analysis of ultracapacitor Concept of material composition modeling, constructional issues and selection of other parameters has been rarely addressed by the researchers [5], [9].

This paper is organized as follows; Section II presents description of sandwich type of binder free ultracapacitor structure used during experimentation. Section III deals with the implementation of design of experiment methodology and Section IV analyze the model. Finally section V concludes the paper.

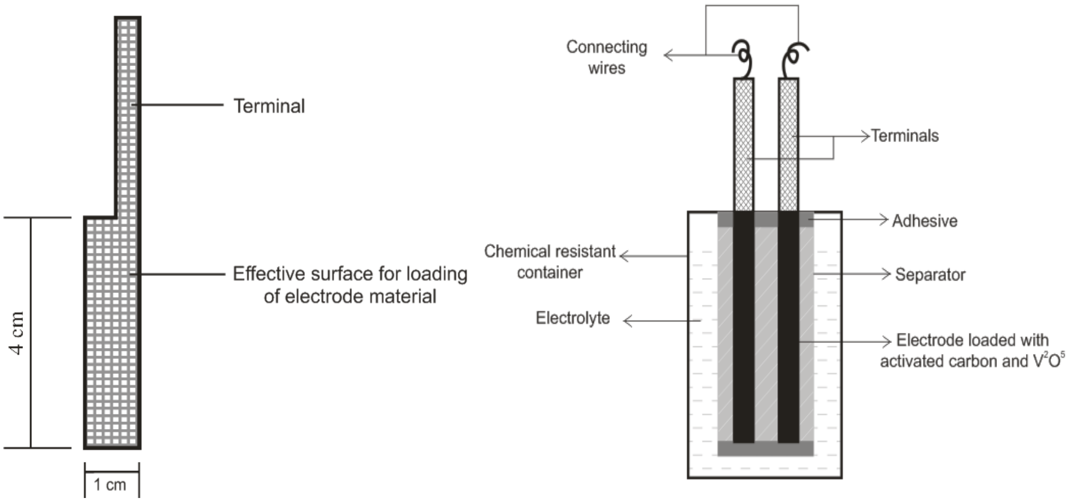
2. Construction of Ultracapacitor

Electrode making process is complicated and requires proper selection of materials and then, the deposition of the electrode material on current collector is a process which require a lot of precision [10]. There are many structures of ultracapacitor being used like rolled, stacked type and flexible type. Rolled type capacitors are feasible for high values of capacitance. This conventional ultracapacitors are heavy bulky, and it is still a challenge to achieve high efficiency miniaturized, energy-storage devices that are compatible with the flexible/wearable electronics [1].

Stacked type structure is used as it is the most suitable structure for low values of ultracapacitors. Generally, binders such as PTFE (Poly Tetra Floro Ethylene) or Nafion are used to hold the electrode material on current collector. In stacked type of ultracapacitor structure, it is found that life of the ultracapacitor device gets affected due to poor quality of electrode material binding on current collector. Therefore, sandwiched type of ultracapacitor structure is used, in which current collector and electrode material is sandwiched between alternate layers of separator pieces. The detailed structure is shown in Fig. 1. The advantages of this type of structure are: 1) suitable for rectangular structure and its packing efficiency is high 2) low cost 3) low internal resistance 4) easy to prepare.

But it is suffers one major drawback that, the cavity effect reduces the life as well as the performance of the device. This cavity effect leads to formation of air gaps between electrode material and separator pieces, which is undesirable. In order to account for these air pockets a large amount of pressure is applied at the time of combining and pasting the loaded electrode and the separator pieces.

Polyethyene separator is used as separator with 40% porosity. Vanadium pentaoxide and activated carbon (Vulcan XC 72/YP 50) is used in the weight ratio of 1:1 as an electrode material. Stainless steel SS316 wire mesh, having 6400holes/inch^2, of area 4 sq. cm (4cm X 1cm) is used as a current collector. Potassium sulphate of 0.65 molarity is used as an electrolyte. Araldite (epoxy resin) is used as adhesive material, which has high acidic, electrical and heat resistive properties, for sealing of electrode structure.



a b

Fig. 1 (a) Current collector of ultracapacitor (b) Sectional view of the Ultracapacitor

3. Implementation of Design of Experiment Methodology

Some statistical methods like , response surface methodology, fractional factorial, full factorial, central composite design etc. can be implementation on ultracapacitor [3]. Ultracapacitor modeling involves the study of "role of electrode materials and electrolytes" in charge storage mechanism [10] [11]. However, to study the complete behavior of the system with minimum number of trials, one has to use the statistical method like design of experiment methodology. Design of experiments includes a series of tests in which changes are made to the input variables of a system and the effects on response variables are measured. Experimental design method helps in reducing the amount of data collected and gives maximum information. The design of experiments specifies the particular setting levels of the combinations of factors at which the individual runs in the experiment are to be conducted [3].

In our trials, the input variables are as mentioned in Table 1 which were found to be the probable factors affecting the value of capacitance. These parameters were obtained from literature available on ultracapacitor. By applying various filters like fixed factors, uncontrollable factors and variation of one parameter at a time, only three factors which are associated with electrodes of ultracapacitor i.e. type of activated carbon, ultra sound mixing time which reflects the quality of electrode material mixing and quantity of electrode material loading on stainless steel current collectors loading for stabilized modelling method i.e. design of experiment methodology were considered. Only three parameters were chosen to reduce the number of trials of design of experiment methodology. Optimization of electrode parameters is done through design of experiment modelling. Optimization of electrolyte parameter is in progress.

Table 1 shows the possible factors that can affect the capacitance of the ultracapacitors. Only three parameters i.e. a) the type of activated carbon b) ultrasonic mixing time which reflects the quality of electrode material mixing c) loading of electrode material on stainless steel collector current, were considered.

Table 1. Possible input factors affecting capacitance

Electrolyte	1) Strength of electrolyte (potassium sulphate) 2) Impurities in electrolyte
Electrode	1) Impurity in electrode material 2) Type of metal oxide 3) Cavity effect 4)Loading of electrode material 5) Activated carbon with different Specific surface area
Electrode making process	1) Pressure on electrode 2) Mixing method 3) Mixing method 4) Adhesive used 5) Separator material used
Current collector	1) Number of holes per unit area of wire mesh 2) Thickness of wire mesh

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Two types of activated carbon that are used are Vulcan XC-72 and YP-50 of kuraray chemical, US. The time taken for ultrasonic mixing is the second parameter and the timings were 15 minutes and 2 hours. The third parameter used is the amount of electrode material on collector current. The electrode material loading selected are $7.5 mg/cm^2$ and $32.5\ mg/cm^2$.

By using these three parameters, eight combinations were made. MINITAB software is used to get statistical model as given by equation 1 of the device using design of experiment methodology. Various output parameters such as capacitance, internal resistance, pulse current and self-discharge etc., which can be considered in design of experiment methodology. However, amongst them capacitance is taken as the main output parameter because in the application of ultracapacitor the ultimate parameter that matters is the capacitance.

Table 2 Parameters associated with electrode of ultracapacitor for design of experiment trials

Input Parameters	A	B	C
System Parameter	Activated carbon type	Ultrasonic mixing time	Loading of electrode material on current collector
Lower value (coded value -1)	Vulcan XC-72	15 minutes	$7.5 mg/cm^2$ of electrode area
Higher value (coded value +1)	YP- 50	2 hours	$32.5\ mg/cm^2$ of electrode area

For the calculation of capacitance, following equation generated by MINITAB software is used:

$$Capacitance = 0.38A-0.13B+0.5C+0.23AB-0.52AC+0.47BC-0.2865ABC$$

This equation is also useful in finding the value of the parameters if we know the values of capacitance.

4. Analysis Of Ultracapacitor From Design Of Experiment Model

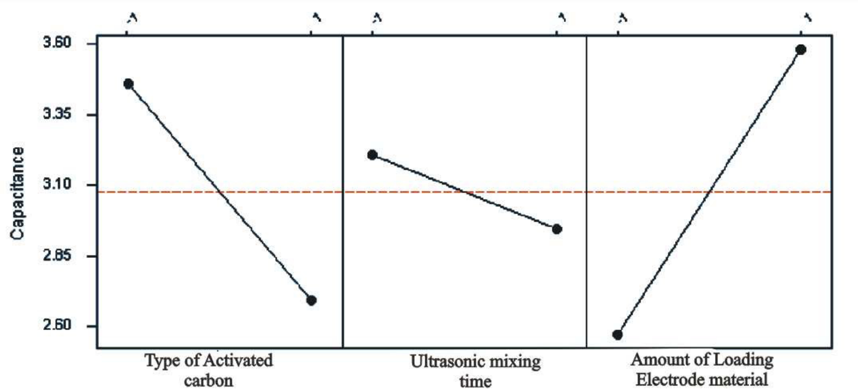

Fig. 2. Individual plot of capacitance

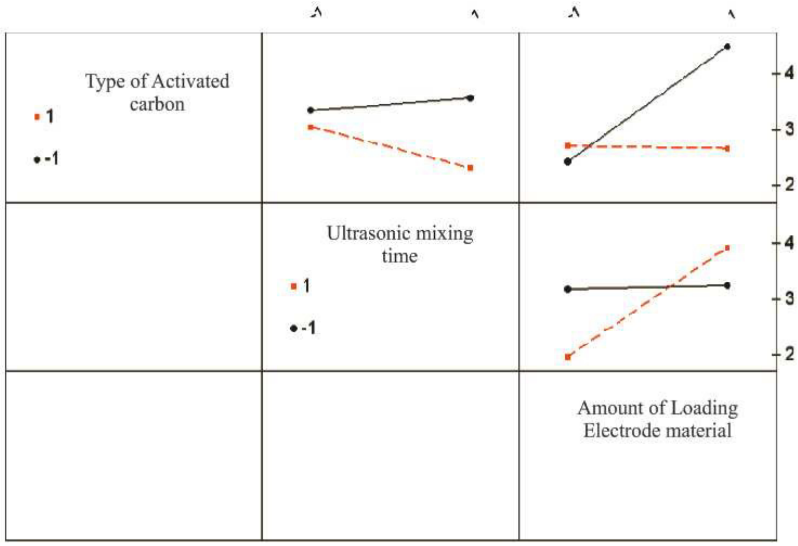

Fig. 3. Interaction effect plot

From Fig.2, it can be concluded that among Vulcan XC and YP-50, Vulcan XC gives higher capacitance value than YP-50. Capacitance hardly depends on ultrasonic mixing time which reflects the quality of electrode material mixing and it also depends on the quantity of loading of electrode material on current collector. For electrode material loading on current collector of $32.5 gm/cm^2$ capacitance is maximum.

Fig. 3 is showing interaction plot for capacitance for different parameters. It shows that type of activated carbon does not have any dependency on ultrasonic mixing time which reflects the quality of electrode material mixing. Type of activated carbon used and loading quantity has a little dependency. Ultrasonic mixing time and loading quantity depends on each other.

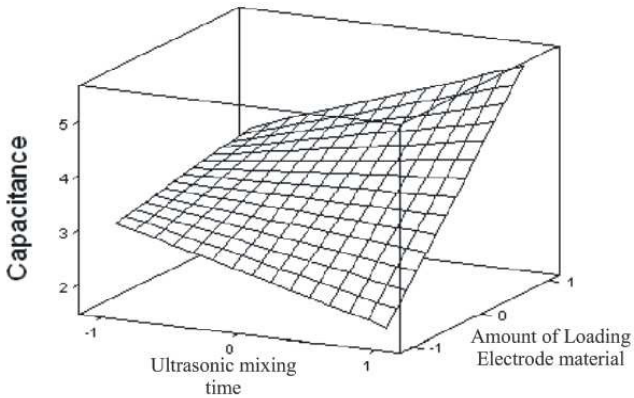

Fig.4. Surface plot of capacitance when YP-50 is used as electrode material

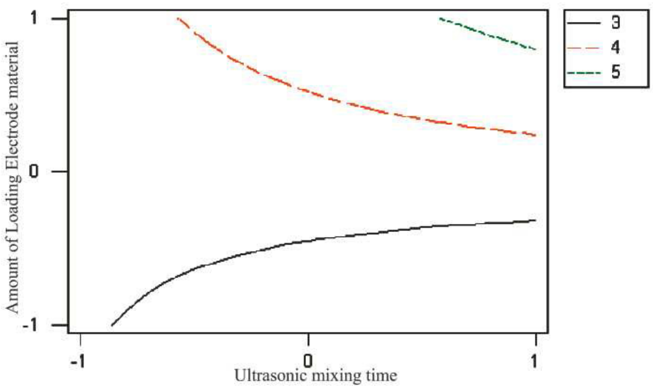

Fig. 5. Contour plot of capacitance when YP-50 is used as electrode material

From Fig. 4 and Fig. 5, it is clearly seen that when ultrasonic mixing time is maximum i.e. 2hours and loading quantity is maximum i.e. 32.5mg/cm^2 capacitance is maximum. This can also be seen from contour plot of capacitance where we are getting highest peak.

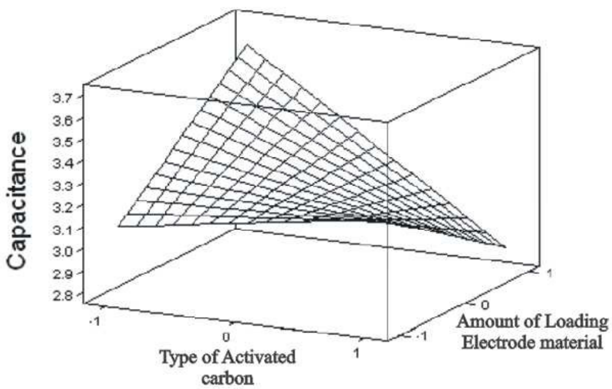

Fig. 6. Surface plot of capacitance when ultrasonic mixing time is maximum i.e. 15 minutes

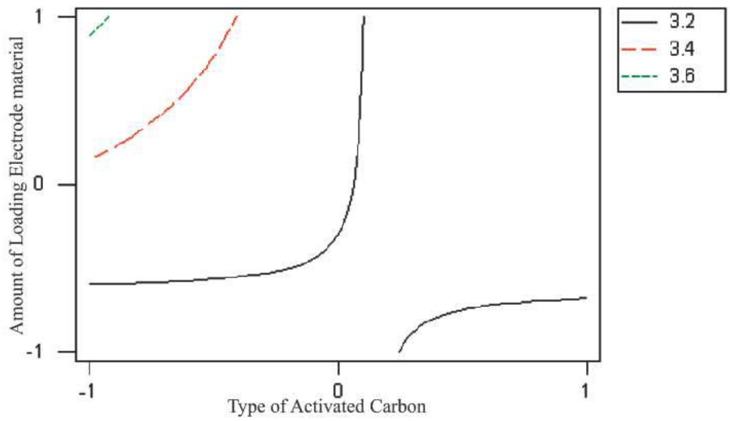

Fig. 7. Contour plot of capacitance when ultrasonic mixing time is maximum i.e. 15 minutes

Fig. 6 and Fig. 7 is denoting surface and contour plot of capacitance, from which it is seen that when type of activated carbon is Vulcan XC-72 and loading quantity is 32.5mg /cm2 highest peak, is obtained and hence maximum capacitance of 3.6F is obtained.

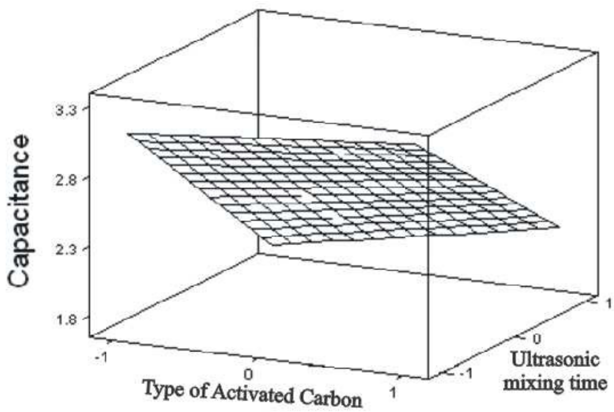

Fig. 8. Surface plot of capacitance when loading of electrode mater on collector current is $7.5mg/cm^2$

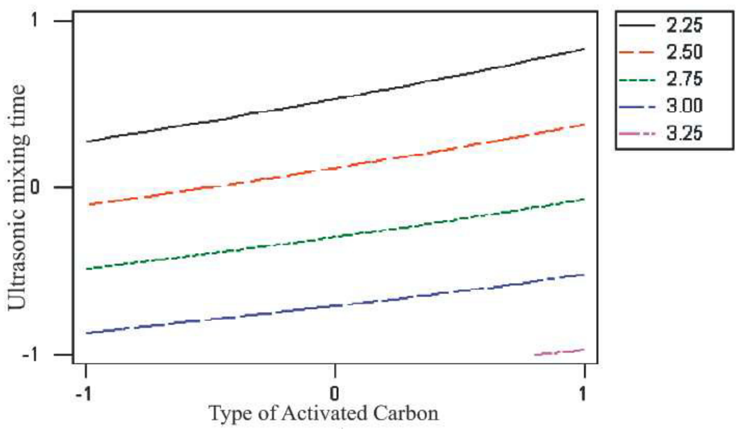

Fig. 9. Contour plot of capacitance when loading of electrode mater on collector current is $7.5\ mg/cm^2$

Fig. 8 and Fig. 9 show that when the amount is electrode material used is 32.5 mg/cm^2 is kept constant, then the value of capacitance varies from 2.25F to 3.35F. It is highest when the ultrasonic mixing time is 15 minutes and activated carbon used is YP-50.

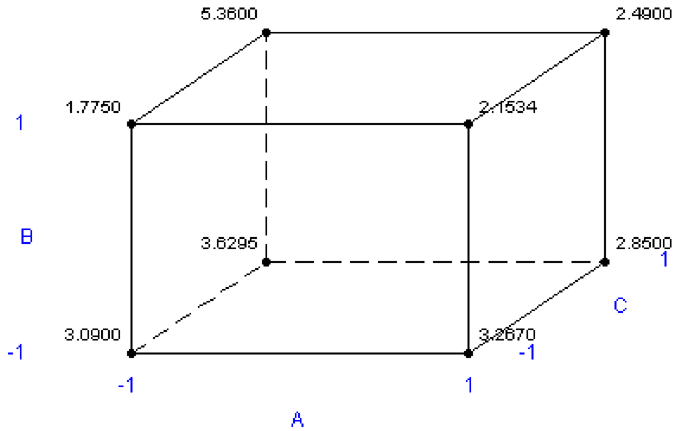

Fig. 10. Cube Plot for Capacitance

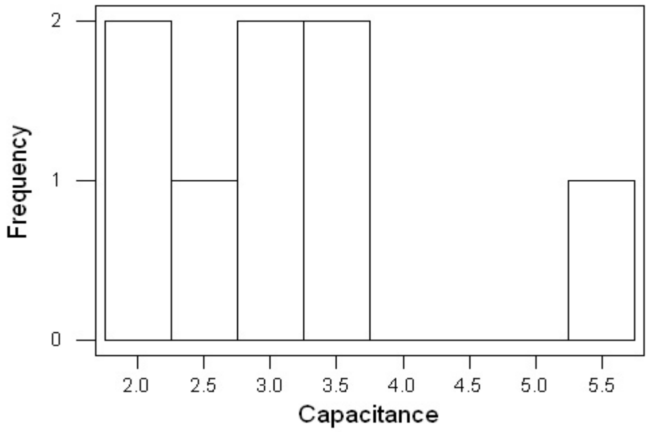

Fig.11. Frequency Distribution Graph for Capacitance of all the combinations

From Fig.10, it can be easily observed that the highest value of capacitance obtained is 5.36 F when Vulcan XC is used with loading of 32.5 mg/cm^2 and ultrasonic mixing time of 2 hrs. And the lowest value of capacitance obtained is 1.77F when YP-50 activated carbon is used with 7.5 mg/cm^2 and ultrasonic mixing of 15min.

Fig.11 shows that frequency of the capacitance value obtained is higher between 2F and 4F. But in only one case, the capacitance value is beyond 5F which indicates that with appropriate input parameter i.e. A, B and C (Refer Table 2), it is possible to obtained high value of capacitance.

5. Conclusions

It was observed that higher loading of the electrode material on current collector is desired as it gives higher capacitance over the wider range of variation in ultrasonic mixing time and type of activated carbon. Vulcan XC-72 with higher electrode material loading gives higher capacitance. Ultrasonic mixing time is not much effective for the various electrode material loading and varying types of activated carbon. Higher material loading cause highly uneven surface of electrode, which results in more gaps formed for charge accumulation resulting higher capacitance. So care must be taken while loading the electrode material on the current collector. Maximum capacitance was obtained as 3.5F when Vulcan XC-72 is used with ultrasonic mixing time of 15 minutes and loading of electrode material on collector current is high i.e. 32.5 mg/cm^2. Hence, with our research work, we have been able to find the parameters which really affect the capacitance. Metal oxide particle size and activated carbon particle size matching is playing key role in increasing capacitive value. Other output parameters such as equivalent series resistance and pulse current also important and can be analysed using the design of experiment methodology.

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